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TRANSMITTAL LETTER

The Assistant Commissioner for Patents  
Washington, D.C. 20231

**ATTN: BOX PATENT APPLICATION**

Sir:

Transmitted herewith for filing is the patent application  
of:

INVENTORS: Kevin Schell,  
John B. Rowen, and  
Anthony S. Camarota

**FOR: Flame Retardant and Smoke Supressive Additive Powder for  
Polymeric Thermoplastics and Thermoset Resins,**

Enclosed are:

- ☐ [14] pages of specification, claims and abstract
- ☐ [0] sheets of formal drawings
- ☒ [X] Declaration and Power of Attorney
- ☒ [X] Assignment of the application to Mitsubishi Electric Information  
Technology Center America, Inc.
- ☐ [ ] Information Disclosure Statement
- ☐ [ ] Preliminary Amendment

The filing fee is calculated as follows:

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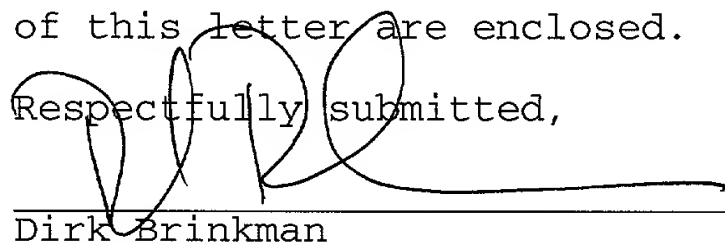
	NUMBER FILED	CLAIMS AS FILED NUMBER EXTRA	LARGE ENTITY	AMOUNT
Basic Fee	12	0	\$ 345.00	\$ 345.00
Total Claims	12	-20 =	x18.00	0.0
Independent Claims	2	-3 =	x78.00	0.0
Assignment Recording Fee			40.00	40.00
Multiple Dependent Claim Fee			260.00	
Other				
			TOTAL FEE	\$ 385.00

- [X] Please record the accompanying Assignment.
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All future correspondence should be addressed to:

**Mr. Anthony Camarota,  
Avtec Industries  
15 Broads Street, Hudson, Ma. 01749**

Duplicate copies of this letter are enclosed.

Respectfully submitted,  


By: Dirk Brinkman  
Reg. No.: 35,460  
Attorney for Assignee

**Avtec Industries  
15 Broads Street, Hudson, Ma. 01749**

09521074-030700

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**STATEMENT CLAIMING SMALL ENTITY STATUS**  
**(37 CFR 1.9(f) & 1.27(c))--SMALL BUSINESS CONCERN**

Docket Number (Optional)

Applicant, Patentee, or Identifier: Kevin Schell  
Application or Patent No.: 09/-  
Filed or Issued: March 7, 2000  
Title: Flame Retardant and Smoke Suppressing Additive Powder  
for Polymeric Thermoplastics and Resins

I hereby state that I am

- ☐ the owner of the small business concern identified below.  
☒ an official of the small business concern empowered to act on behalf of the concern identified below.

NAME OF SMALL BUSINESS CONCERN Avtec Industries

ADDRESS OF SMALL BUSINESS CONCERN 15 Broad Street  
Hudson Ma 01749

I hereby state that the above identified small business concern qualifies as a small business concern as defined in 13 CFR Part 121 for purposes of paying reduced fees to the United States Patent and Trademark Office. Questions related to size standards for a small business concern may be directed to: Small Business Administration, Size Standards Staff, 409 Third Street, SW, Washington, DC 20416.

I hereby state that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention described in:

- ☒ the specification filed herewith with title as listed above.  
☒ the application identified above.  
☐ the patent identified above.

If the rights held by the above identified small business concern are not exclusive, each individual, concern, or organization having rights in the invention must file separate statements as to their status as small entities, and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern, or organization having any rights in the invention is listed below.

- ☐ no such person, concern, or organization exists.  
☐ each such person, concern, or organization is listed below.

Separate statements are required from each named person, concern or organization having rights to the invention stating their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

NAME OF PERSON SIGNING ANTHONY S. CAMAROTA

TITLE OF PERSON IF OTHER THAN OWNER Vice President

ADDRESS OF PERSON SIGNING 15 BROAD STREET HUDSON, MA. 01749

SIGNATURE Anthony S. Camarota DATE 3-6-00

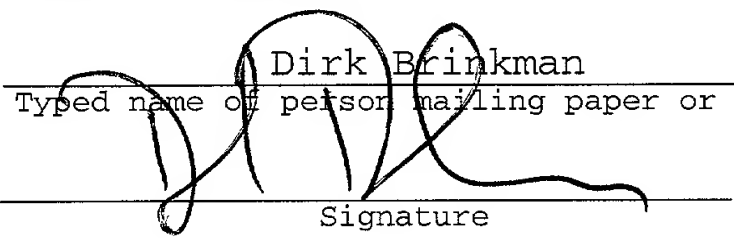
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Dirk Brinkman

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=====

APPLICATION FOR UNITED STATES LETTERS PATENT

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Title: Flame Retardant and Smoke Supressive  
Additive Powder for Polymeric  
Thermoplastics and Thermoset Resins

Inventors: Kevin Schell,  
John B. Rowen, and  
Anthony S. Camarota

002030 1201500

## **Flame Retardant and Smoke Suppressive Additive Powder for Polymeric Thermoplastics and Thermoset Resins**

### **Field of the Invention**

This invention relates to flame retardant and smoke suppressive compositions, and  
5 more particularly to powdered compositions for mixing with resins.

### **Background of the Invention**

Typically, resins are petroleum by-products that have potentially very harmful  
10 burning characteristics, i.e., high flammability at relatively low temperatures, very  
toxic and acrid smoke, and rapid destructive flame spread. It is well known in the  
art that the flammability of curable resins can be reduced by incorporation of  
flame retardant agents. However, when additives are intended for use with curable  
resins, a multitude of problems arise.

15 Curable resins are frequently used in the manufacture of reinforced plastics,  
fiberglass laminates, reenforced plastics used as plenums and cable trays used for  
housing electrical wiring. Plastics are also widely used by automobile and aircraft  
manufacturers. The burning behavior of such materials, particularly those that are  
20 to be used in an enclosed situation, are of primary concern. Many reinforced  
plastics can be designed to have a degree of fire resistance. Many additives are  
available which inhibit burning, but unfortunately, many of these compounds give  
off very toxic fumes, such as nitrous oxides, cyanide, halogenated compounds etc.

Many prior art references describe the use of a variety of flame retardant additives, see "*Modern Plastics Encyclopedia*," Vol. 63, No. 10A, McGraw-Hill, Inc., pp. 179-180 (1986). Typical flame retardant agents include reactive or additive  
5 halogenated organic compounds, inorganic fillers, solvents, and special formulations based on phosphorous and ammonium salts.

However, the selection of a suitable smoke suppressant for a curable resins is not predictable. Selection is particularly difficult when flame retardants are employed,  
10 exacerbated by the complex interaction between the resin and the flame retardant agent. Although efficient in suppressing the rate of combustion of finished products that incorporate the resin, most flame retardants tend to affect adversely one or more key properties of the resin. For example, many flame retardant additives are ineffective at producing low density and low toxicity formulations.

15 It is well known, that the flame retardant and smoke suppressive properties of additives in resin formulations varies greatly with the nature of substrate. This is particularly true for intumescent compositions because the rapid formation of a protective char is highly dependent upon such factors as the combustion  
20 temperature, and the viscosity of the melt formed by the burning substrate.

Other considerations can also come into play, even where the properties of the retardant and suppressive properties of the composition are optimum. These considerations include the effect of the additive on the physical properties, color  
25 and molding characteristics of the base resin.

U.S. Patent No. 3,293,327 describes the production of bicyclic phosphites, phosphonates, thiophosphates, and selenophosphates. These compositions are said to be stabilizers for vinyl halide resins. They are said to be useful as heat stabilizers for vinyl chloride resin, and as antioxidants for fats and oils.

5

Intumescent, fire-retardant coating compositions containing carbonifics, film-forming binders and phosphorous materials are well known in the art. U.S. Patent Nos. 3,562,197; 3,513,114; 4,009,137; 4,166,743 and 4,247,435 disclose such compositions containing ammonium polyphosphates as the phosphorous containing material.

10

U.S. Patent No. 3,654,190 discloses an intumescent paint comprising a resinous binder, a blowing agent, a phosphorous containing material, a source of chlorine a solvent, an anti-settling agent, a pigment and a surfactant.

15

U.S. Patent No. 3,969,291 describes the use of an amide polyphosphate condensate as a fire-retardant additive in an intumescent coating composition. U.S. Pat. No. 3,914,193 discloses the similar use of a crystalline form of melamine pyrophosphate.

20

U.S. Patent No. 4,801,625, describe a flame resistant composition having (1) an organic polymeric substance in intimate contact with (2) a bicyclic phosphorous compound, and (3) a gas producing compound. The patent is silent on the use of bicyclic compounds to attain smoke suppressed flame retardant thermoset

25

compositions.

U.S. Patent No. 5,356,568 describes a solvent-based heat-resistant and fire-retardant coating containing carbonifics, film-forming binders, phosphorous materials. Also described is an application where the coating sprayed on steel and aluminum plates using a gravity flow gun. Not described are any smoke retardant properties, nor the use of the coating with resins or polymer plastics.

The development of additives for use with resins remains a highly empirical art. The predictability of the behavior of the final composition is rare to non-existent. The prior art has largely concentrated on developing highly specific additive combinations for particular resins and end-uses.

Therefore, it is desired to provided an additive composition which exhibits a greater latitude in dispersability, flame retardation, and smoke suppression. It is also desired to provide an additive for use in a variety of resins.

### Summary of the Invention

A flame retarding and smoke suppressing additive powder that can be mixed with curable or hardenable resins, polythermic plastics , and other thermal oxidizable petrochemical based compounds and derivatives. The powder includes a carbonific material, a heat activated blowing agent, a heat activated halogen material, a phosphate material, and an inorganic material.

The additive powder, when added to a curable or hardenable resin, forms a mixture where the additive powder is about 20-30%, by weight, of the mixture.



The resin can be styrenic, olefinic, acrylic, cellulosic, polyester, or polyamide such as are commonly used in the manufacture of fiberglass reinforced structures and moldable plastics.

## 5 Detailed Description of the Preferred Embodiment

### Additive

The invention provides a flame retardant and smoke suppressive powder that can be added to resins and used in manufacturing processes. When the powdery additive according to the invention is mixed with a resin, the propensity of the otherwise untreated resin to combust, generate toxic smoke, and transmit heat when exposed to an open flame or excessive heat is significantly reduced.

The powdered composition according to the invention is "active." By being active, the composition has a latent ability to intumesce or foam when a specific temperature is reached. This is due to the nature of a blowing agent, which is a part of the composition. In a preferred embodiment, that temperature of flame or heat retardation is 250 degrees Centigrade. At this temperature, and above, the cured or hardened resin/composite structure resists combustion, self-extinguishes without the direct application of a flame extinguisher, and produces a smaller quantity of less toxic smoke than similar parts made without use of the invention.

In a preferred embodiment, the composition, by weight, of the additive formulation is:

	<u>Ingredient</u>	<u>Wgt. % Range</u>	<u>Function</u>
	a) Dipentaerythritol	10.0-12.0	carbonific
	b) Melamine	15.5-17.5	blowing agent
	c) Chlorinated Paraffin - 40%	4.0- 6.0	halogen material
5	d) Chlorinated Paraffin - 70%	8.0-11.0	halogen material
	e) Ammonium polyphosphat	27.5-29.9	phosphorous
	f) Tris(betachloroethyl)phosphate	2.5- 4.5	phosphorous
	g) Silica flour (120 mesh	8.5- 10.5	inorganic
	h) Glass beads- Zeosphere	2.5- 4.5	inorganic
10	i) Calcium aluminate cement	12.5- 14.5	inorganic

The ingredients of the additive are mixed blended at ambient (room) temperature until fully incorporated. The additive in its final form is a white fine powder.

15 Each of the components of the composition of the present invention contributes a specific property to the formulation and each is critical to the success of the invention in yielding a reduced propensity for the resin so treated to burn, smoke, generate toxic gases or transmit heat.

## 20 **Carbonific**

In a preferred embodiment, the primary carbonific of the flame retardant composition is dipentaerythritol or tripentaerythritol. The carbonific, simply stated, is a source of carbon. It is the purpose of the carbonific to produce a carbon char layer to insulate the underlying uncombusted resin and finished structure  
25 from greater thermal damage. It should be understood, that the resin itself with which the flame retardant additive is mixed can also be a source of carbon, and,

thus, a carbonific. In the case where the resin is a carbon, the amount of primary carbonific a) can accordingly be adjusted downward if the resin is to be relied upon as a carbonific for the combustion process. In other embodiments, the carbonific material carbonific material can be selected from the group consisting of dipentaerythritol, pentaerythritol, pentaerythritol polyurethane, phenol, triethylene glycol, resorcinol, inositol, sorbitol, dextrin, and starch.

### Blowing Agent

The blowing agent is primarily comprised of melamine. Heat decomposition of the melamine produces ammonia, urea, water, carbon dioxide, etc. These gases act to expand the volume of the resin during combustion. The gases help produce a multicellular foamy resin which insulates and protects the resin and structure from additional heat.

### Halogen

The halogen containing material is preferably a chlorinated paraffin, most preferably, a mixture of a chlorinated paraffin containing about 70%, by weight, of chlorine and a chlorinated paraffin containing about 40% by weight, of chlorine.

The weight ratio of 70% chlorinated paraffin to 40% chlorinated paraffin is preferably from about 1:2.

The halogen containing material serves several functions. It acts as a carbonific, a blowing agent and a fire snuffing agent. On exposure to heat it is reduced to a char (carbonific) liberating halogen gas (blowing agent) which combines with or scavenges free-radicals generated during rapid oxidation, thus, aiding in the extinguishing of flames (fire snuffing agent). In other embodiments, the heat

activated blowing agent is selected from the group consisting of urea, butyl urea, dicyandiamide, benzene sulfonyl-hydrazide, melamine, chloroparaffin, guanidine, and glycine.

## 5 Phosphorous

The phosphorous containing materials are ammonium polyphosphate and tris (betachloroethyl) phosphate at approximately a 10:1 ratio. The phosphorous containing material serves as a catalyst to activate the melamine blowing agent and, in addition, reacts with the carbonific, further consuming it and generating carbon. Under the influence of heat from a fire or otherwise, the catalyst decomposes, yielding phosphoric acid. The reactive phosphoric acid produced by the breakdown of the catalyst reacts with both the amine function of the melamine and the hydroxy function of the carbonific to produce water. In addition, under the applied and generated heat, the organic components of the resin composite are degraded producing yet additional insulating char. In other embodiments, the phosphate material is selected from the group consisting of ammonium polyphosphate, tris(2,3-dibromopropyl) phosphate, tris(beta-chloroethyl) phosphate, guanidine phosphate, urea phosphate, melamine phosphate, monoammonium phosphate, diammonium phosphate, and mixtures thereof.

## Inorganic

The heat resistant inorganic material can include a mixture of any suitable heat resistant materials, e.g., silica flour, heat and flame resistant material, e.g., glass beads, etc, and calcium aluminate cement. The inorganic material is also multifunctional. In a resin composition, the inorganic material can enhance the overall strength and impact resistance of a finished product made with the

composite resin. As an advantage of the invention, the inorganic material can be tailored for adhesion, flame retardance, and flexibility. The inorganic can also serve as a heat deflector. At extremely high temperatures, the inorganic material melts to form a frit, which is highly insulative and heat resistant.

5

## Resin

10 The relative weight percentage of the additive to the resin is 20% to 35% based on the amount of flame retardation and smoke suppression that is required. In one application, the additive is mixed with the resins at ambient (room) temperature, and blended until fully incorporated. The additive can also be applied to cured parts, or incorporated directly into resin-based systems.

15 Unlike the prior art, where the additives are usually highly specific additive combinations for particular resins and end-uses, the additive according to the invention can be mixed with a broad range of classes of resins, a large number of end-uses, and manufacturing processes.

20 For example, the resin can be a curable or hardenable material, such as a styrenic, olefinic, acrylic, cellulosic, polyester, or polyamide or any other class of resin. In a preferred embodiment, the resin is a styrenic such as those commonly used in the manufacture of fiberglass, reinforced structures.

25 The resin can also be any class of resins used in resin transfer moldings (RTM), bulk moldings, sheet moldings, fiber reinforced polymer pultrusions, compression moldings, vacuum injection moldings, assisted resin transfer moldings (VARTM),

pressure bag moldings, hand lay-ups and spray-ups, filament windings a, cold press moldings, continuous laminating, rotational moldings, encapsulations and preimpregnations.

## 5 Test Results

ASTM E-162 (Surface Flammability of Materials Using a Radiant Heat Energy Source) Radiant Panel Test for the surface burning flammability of materials are used by many authorities to determine fire hazards. It is generally accepted that the higher the flamespread numbers the greater the fire hazard. Comparative results for the ASTM protocols are listed in Table A.

**Table A**

Property	Invention	Typical Prior Art
Flame Spread Ratio	10.6	25+
Smoke	3.9	300+
Toxicity	None	High

Although the invention has been described by way of examples of preferred embodiments, it is to be understood that various other adaptations and modifications may be made within the spirit and scope of the invention. Therefore, it is the object of the appended claims to cover all such variations and modifications as come within the true spirit and scope of the invention.

## Claims

We claim:

- 1 1. A flame retarding and smoke suppressing additive powder, comprising,  
2 by weight:
  - 3 a carbonific material 10.0-12.0%;
  - 4 a heat activated blowing agent 15.5-17.5%;
  - 5 a heat activated halogen material 12.0- 17.0 which forms a fire  
6 extinguishing halogen gas under heat;
  - 7 a phosphate material 30-33.4% which forms water and phosphorous  
8 when reacting with one or more of the remaining ingredients in the powder  
9 under heat; and
  - 10 an inorganic binder 23.5-29.5%.
- 1 2. The powder of claim 1 wherein the carbonific material carbonific material  
2 is selected from the group consisting of dipentaerythritol, pentaerythritol,  
3 pentaerythritol polyurethane, phenol, triethylene glycol, resorcinol, inositol,  
4 sorbitol, dextrin, and starch.
- 1 3. The powder of claim 1 wherein the heat activated blowing agent is  
2 selected from the group consisting of urea, butyl urea, dicyandiamide,  
3 benzene sulfonyl-hydrazide, melamine, chloroparaffin, guanidine, and  
4 glycine.

- 1 4. The powder of claim 1 wherein the heat activated halogen material is  
2 selected from the group of chlorinated paraffin - 40% and chlorinated  
3 paraffin - 70%.
- 1 5. The powder of claim 1 wherein the phosphate material is selected from  
2 the group consisting of ammonium polyphosphate, tris(2,3-dibromopropyl)  
3 phosphate, tris(beta-chloroethyl) phosphate, guanidine phosphate, urea  
4 phosphate, melamine phosphate, monoammonium phosphate, diammonium  
5 phosphate and mixtures thereof.
- 1 6. The powder of claim 1 wherein the inorganic binder is selected from the  
2 group consisting of calcium aluminate cement, silica flour, and glass beads.
- 1 7. The powder of claim 1 further comprising a mixture with a resin wherein  
2 the powder is in the range, by weight, of 20-30% and the resin is in the  
3 range, by weight, of 70-80%.
- 1 8. The powder of claim 7 wherein the resin is selected from the group of  
2 styrenic, olefinic, acrylic, cellulosic, polyester, and polyamide.
- 1 9. The powder of claim 7 wherein the resin is a thermoset resin.
- 1 10. The powder of claim 7 wherein the resin is a curable resin.



11. The powder of claim 8 wherein the resin is selected from the group of resins consisting of resin used in transfer moldings, bulk moldings, sheet moldings, fiber reinforced polymer pultrusions, compression moldings, vacuum injection moldings, assisted resin transfer moldings, pressure bag moldings, hand lay-ups and spray-ups, filament windings, cold press moldings, continuous laminating, rotational moldings, encapsulations and preimpregnations.

1 12. A flame retarding and smoke suppressing additive powder for mixing  
2 with resins comprising, by weight:

3 10.0-12.0% of a carbonific comprising of dipentaerythritol,  
4 dipentaerythritol, pentaerythritol, pentaerythritol polyurethane, phenol,  
5 triethylene glycol, resorcinol, inositol, sorbitol, dextrin, or starch;

6 15.5-17.5 of a blowing agent comprising malamine;

7 12-19.0 of a halogen containing material comprising a chlorinated  
8 paraffin;

9 30-33.4% of a phosphorous containing material which is selected  
10 from the group consisting of ammonium polyphosphate, tris(2,3-  
11 dibromopropyl) phosphate, tris(beta-chloroethyl) phosphate, guanidine  
12 phosphate, urea phosphate, melamine phosphate, monoammonium  
13 phosphate, diammonium phosphate; and mixtures thereof;

14 23.5-29.5% of an inorganic material is selected from the group  
15 consisting of calcium aluminate cement, silica flour, and glass beads.

### **Abstract of the Disclosure**

A flame retarding and smoke suppressing additive powder that can be mixed with resins includes a carbonific material, a heat activated blowing agent, a heat activated halogen material, a phosphate material, and an inorganic material. The additive powder, when added to a curable or hardenable resin, forms a mixture where the additive powder is about 20-30%, by weight, of the mixture. The resin can be styrenic, olefinic, acrylic, cellulosic, polyester, or polyamide such as are commonly used in the manufacture of fiberglass reinforced structures and moldable plastics.

**DECLARATION AND POWER OF ATTORNEY**

**DECLARATION:**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe, the below named inventors are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention for entitled **Flame Retardant and Smoke Supressive Additive Powder for Polymeric Thermoplastics and Thermoset Resins**, the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims. I acknowledge the duty to disclose information which is material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby declare that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:**

On behalf of Avtec Industries, Assignee of my entire right, title and interest, I hereby appoint the following attorney with full power of substitution to act exclusively for Avtec Industries to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Dirk Brinkman, Reg. No. 35,460.

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Inventor's Full Name:	Anthony S. Camarota
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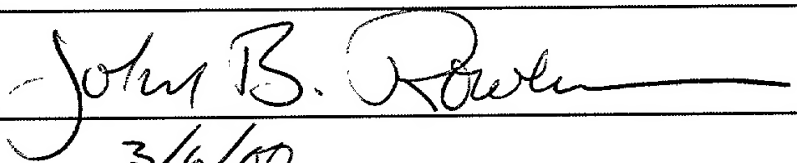
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